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THE RAPID PRECIPITATION

OF

LEAD AND MERCURY

IN THE

ELECTROLYTIC WAY.

THESIS

PRESENTED TO THE FACULTY OF THE DEPARTMENT OF
PHILOSOPHY OF THE UNIVERSITY OF PENNSYLVANIA
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

BY

RALPH OGDEN SMITH, A.M.,

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THE RAPID PRECIPITATION OF LEAD AND MERCURY IN THE ELECTROLYTIC WAY.

DETERMINATION OF LEAD FROM A NITRIC ACID ELECTROLYTE.

From a neutral or slightly acid solution of a lead salt an electric current precipitates metallic lead upon the cathode and a hydrated dioxide[1] upon the anode.

Early in the annals of electro-analysis it was known[2] that in the presence of a definite excess of nitric acid all the lead could be thrown down as dioxide upon the anode. This behavior of lead solutions toward the current, has been utilized by chemists in making separations of lead from other metals which are not deposited in this way upon the anode.[3]

In this connection it is of interest to notice the manner in which different chemists have treated the deposits thus obtained before calculating its lead content. In a communication, "von der Mansfeldischen Ober-Berg- und Hutten- Direction,"[4] it is pointed out that the deposit upon the anode is not, under all conditions, lead dioxide, but an indefinite hydrated dioxide of varying lead content, from which the lead cannot be accurately estimated.

W. C. May[5] prefers to rub off this deposit with a rubber-covered glass rod and converts it into lead oxide by gentle ignition, weighing as PbO. His results are excellent, but the method has the disadvantage that it requires considerable manipulation to remove the deposit completely from the anode and in the subsequent filtering, washing, drying and separating from the filter which is ignited separately.

Alfred Riche[6] weighs as PbO_2, after taking the precaution to

[1] Becquerel: Ann. chim. phys. [3], 8, 405.
[2] Luckow: Z. anal. Chem., 19, 4.
[3] Z. anal. Chem., 8, 24; *Ibid.*, 11, 9.
[4] Z. anal. Chem., 11, 13.
[5] Am. J. Sci, and Arts, [3], 6, 255.
[6] Ann. chim. phys. [5], 13, 519.

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wash the deposit three or four times with water, drying at 105°-120° C. Riche worked with quantities of lead varying from 0.002 to 2.0005 grams and his results are very concordant.

Luckow[1] weighs as PbO_2, after washing and drying, no temperature being given.

Schucht[2] does not obtain constant results by drying at 110° C., as suggested by Riche, and he finds by weighing as PbO, as directed by May, that results are satisfactory, but that the platinum anode is attacked when it is ignited in order to determine the traces of hydrated dioxide, which adhere to it and cannot be rubbed off. Schucht dried the deposit at 30°-40° C. for fifteen minutes and then to constant weight over sulphuric acid. An analysis of this product showed the presence of 0.47 to 1.18 per cent of water.

Alexander Classen[3] recommends that the deposits should be dried at 180°-190° C. before weighing. No data are given.

Oscar Piloty,[4] following Classen's directions, obtained good results. He weighed from 0.6940 to 1.0707 grams of PbO_2.

A. Kreichgauer[5] says that it does not make any difference whether the deposits are dried at 110° or 200° C. He points out that there are traces of nitric acid in the deposit and says that by washing twice with absolute alcohol this is removed.

A. Hollard[6] washes the deposit twice with water and then heats gradually to 200° C. After heating at this temperature for fifteen minutes he says the deposit corresponds exactly to the formula PbO_2. Four years later this same chemist writes as follows: "We have found (1) that the analytical factor 0.866 (Pb/PbO_2) is too large and that there is deposited upon the anode, together with PbO_2, a superoxide containing more oxygen than PbO_2; (2) that the proportion of this superoxide is greater as the concentration of lead in the electrolyte diminishes."[7] For example, the analytical factor for a deposit of PbO_2+X weighing 0.0106 gram

[1] Z. anal. Chem., 19, 4.
[2] *Ibid.*, 22, 487.
[3] Ber. Chem. Ges., 27, 164.
[4] Ber. Chem. Ges., 27, 280.
[5] Ber. Chem. Ges., 27, 315.
[6] Ann. de Chim. Anal., 4, 11.
[7] Ann. de Chim. Anal., 8, 164.

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is 0.740, which gradually increases until for a deposit of 10.0000 grams the factor is 0.861.

The formation here of an oxide of lead higher than PbO_2 is hardly probable. This is shown by the work of Schucht, already cited, who allows oxalic acid to act upon the electrolytic PbO_2, dried over sulphuric acid, and from the CO_2 evolved calculates the presence of 98.50 per cent. PbO_2, which figure, coupled with the water content found by Schucht and given above, does not indicate the presence of any oxide higher than PbO_2. Moreover, in the following year Hollard states[1] that by using an anode of platinum, covered with a layer of platinum black, this superoxide formation can be diminished, but not entirely prevented. The analytical factor, under these conditions becomes a constant (0.853) for all concentrations of lead in the electrolyte. It is to be noticed that in the eight determinations from which the analytical factor 0.853 is determined there is a variation between the maximum and minimum of 0.006.

At this point it is of interest to refer to the work of Carnelley and Walker upon "The Dehydration of Metallic Hydroxides by Heat." Under the head of "Hydrate of PbO_2" they write,[2] "precipitated lead dioxide, after drying in the air for ten days, had very nearly the composition $3PbO_2.H_2O$. On heating, it gradually lost water and became dehydrated at about 230°; on further heating its weight remained nearly constant up to 280°, at which temperature it suddenly lost oxygen and was converted into Pb_2O_3." Their work was carried out with 0.7065 gram of $3PbO_2.H_2O$, made by passing Cl through a solution of lead acetate which had been precipitated with a solution of sodium carbonate and the resulting precipitate dried, as indicated above. It would seem within reason that the electrolytic hydrated dioxide of lead should also be heated to constant weight at 230° C. before calculating its lead content.

In addition to the above, most chemists have determined the lead content of the crystallized salt $Pb(NO_3)_2$, and in but one instance[3] is it mentioned that any precautions have been taken to

[1] Ann. de Chim. Anal., 9, 125.
[2] J. Chem. Soc., 53, 85.
[3] Piloty: Loc. cit.

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dry this salt, and in that case no particulars are given. The fact that the lead content calculated from the electrolytic deposit of dioxide agrees with the lead content of this salt is no criterion for the accuracy of the method, as long ago Stas pointed out[1] that this salt was not of definite composition until dried to constant weight at 155° C.

The lead nitrate used in the following experiments was recrystallized once in the presence of lead oxide and twice by precipitation by concentrated nitric acid and then air-dried. A solution of this salt was made up to contain approximately 10 grams of lead per liter. The amount of lead present in 5 cc. and 25 cc. was determined as lead sulphate. Thus in each case the pipettes used were standardized by pipetting out two samples of the required amount into tared porcelain crucibles, adding a slight excess of sulphuric acid, evaporating off the excess of water upon a water-bath and then expelling nitric acid and excess of sulphuric acid upon an asbestos plate till fumes of SO_3 were no longer evolved, keeping the crucibles covered to exclude dust. The crucible was then gently ignited over a Bunsen burner until the bottom was a faint red, cooled in a desiccator and weighed. In order to insure that there had not been any reduction by dust particles the contents of the crucible were moistened with one drop of nitric acid followed by a drop of sulphuric acid, the excess of acid removed as before, the crucible ignited and reweighed. In no case was there loss in weight.

In order to ascertain if it was possible to ignite off all traces of sulphuric acid without the reduction of lead sulphate by gases passing through the crucible, one sample was ignited five times and no loss in weight noted. By carefully revolving the crucible, inclined upon a pipe-stem triangle, over a full Bunsen burner, there is no danger of reduction, at least in the time necessary for the complete expulsion of traces of sulphuric acid.

The following determinations were made with a rotating cathode according to the method of Exner.[2] For details as to apparatus see the work of Exner and also that of Ingham.[3]

[1] "Recherches sur le rapports reciprociques des poids atomique," Brux. 1860, through the Journal für praktische chemie, 1861, 1, 87.

[2] J. Am. Chem. Soc., 25, 896.

[3] *Ibid.*, 26, 1296.

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Determinations of the rate of rapid precipitation of metals as developed in this laboratory[1] show the minimum time necessary for the complete deposition of the metal under consideration. Another proof of its complete deposition is its absence from the solution siphoned off from the deposit. The literature does not show that tests have been made in this way for lead.

In the following experiments the solutions siphoned off from the deposits, together with the wash waters, amounting to 2 liters, were evaporated to dryness, taken up with a little dilute acetic acid with the addition of a few drops of potassium bichromate solution. After standing for several hours considerable precipitates were obtained in all of the following cases: Tables I and II, save with Nos. 5, 6, 7, 12 and 13, whereas in the cases cited but a slight precipitate could be detected. It was filtered off and washed with water. It was yellow in color and dissolved in sodium hydrate solution.

A slight deposit of metallic lead was found upon the cathode in the cases cited, even in the presence of 20 cc. of nitric acid (sp. gr. 1.4). It is true that no perceptible increase in the weight of the cathode could be noticed, but when it was treated with a little dilute acetic acid and tested as above a slight precipitate was obtained. As has been pointed out by Giese,[2] it seems probable that during electrolysis some metal is deposited upon the cathode and that toward the end of the experiment it is gradually dissolved and deposited as dioxide upon the anode. In order to hasten this solution of metal on the cathode the current was interrupted for a short time, five seconds, after the experiment had been going for five minutes and again five minutes before the experiment was ended, at least in all cases where the experiment lasted fifteen minutes.

Giese's view is probably correct, as considerable deposits of lead were noticed in the case of Nos. 1, 2 and 8 where the current had not been interrupted.

At the end of each experiment the acid liquid was siphoned off without interrupting the current, fresh water being introduced to keep the level above the deposit until the ammeter registered zero.

[1] J. Am. Chem. Soc., 26, 1269; *Ibid.*, 26, 1595.
[2] Z. Elektrochem., 2, 601.

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The current was then cut off, the dish removed, its contents washed with absolute alcohol and absolute ether to remove excess of water. It was then dried in an air-bath at 230° C. to constant weight, cooled in a desiccator in the balance room for fifteen minutes, allowed to stand upon the pan in the balance case for a like period and the weight then taken. The deposit was not hydroscopic, for it did not change in weight upon standing in the balance case for two hours.

The deposit was dissolved off the dish with a mixture of oxalic and nitric acids. The dish was cleaned and weighed before each experiment and was found to have lost 0.0002 or 0.0003 gram during each experiment.

RATE OF DEPOSITION OF 0.2867 GRAM OF LEAD DIOXIDE.

Twenty-five cc. of lead nitrate solution gave 0.3635 gram $PbSO_4$, equivalent to 0.2483 gram Pb or 0.2867 gram PbO_2.

Electrolyte.—Twenty cc. HNO_3 (sp. gr. 1.4), 25 cc. $Pb(NO_3)_2$ solution. Total dilution, 115 cc. Solution heated to 60°-70° C. before electrolysis.

TABLE I.

No. of experiment.	Time in min.	PbO_2 found.	Pb calc.	Pb present.	Volts.	N. D_{100} amperes.
1	3	0.2478	0.2146	0.2483	3.7	11.6–11.0
2	6	0.2679	0.2320	0.2483	3.9–3.8	10 –10.8
3	9	0.2807	0.2431	0.2483	3.8	11
4	12	0.2858	0.2475	0.2483	3.7–3.8	10.8–11
5	15	0.2873	0.2488	0.2483	3.7–3.8	11
6	18	0.2873	0.2488	0.2483	3.9	11.2–11
7	15	0.2874	0.2489	0.2483	4.0	13

RATE OF DEPOSITION OF 0.5770 GRAM OF LEAD DIOXIDE.

Twenty-five cc. lead nitrate solution gave 0.3657 gram lead sulphate, equivalent to 0.2498 gram Pb or 0.2885 gram PbO_2.

Electrolyte.—Fifty cc. lead nitrate solution, otherwise the same as for the preceding experiments.

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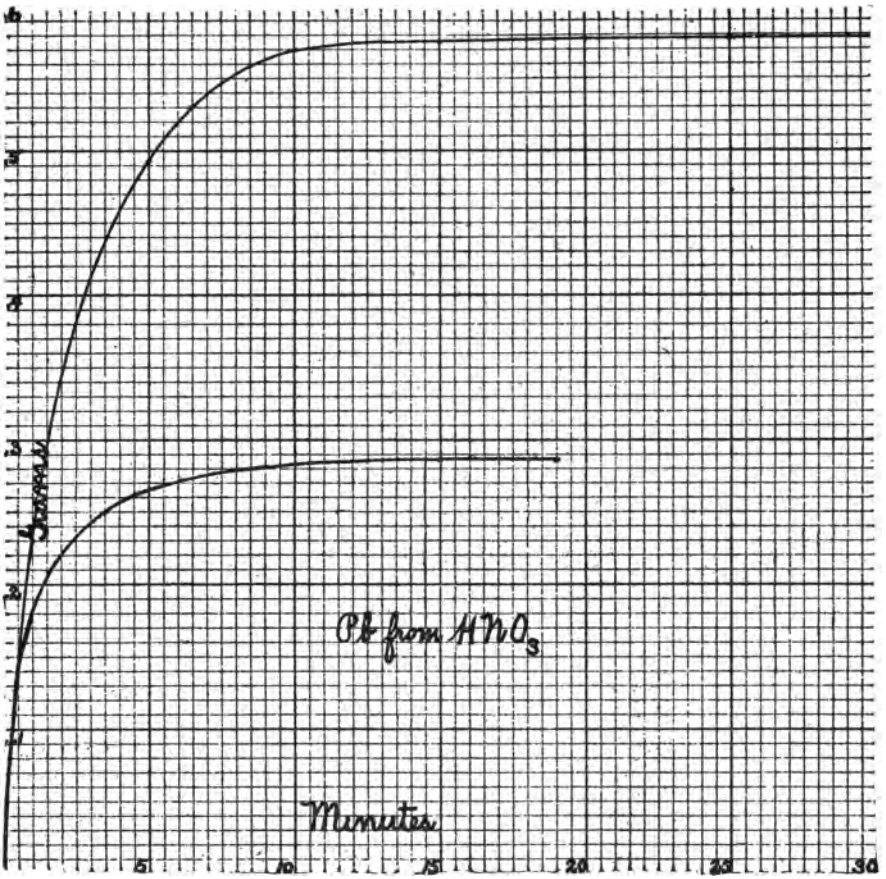

FIG. 1.—Rate of deposition of lead dioxide.

TABLE II.

No. of experiment.	Time in min.	PbO_2 found.	Pb found.	Pb present.	Volts.	N. D_{100} amperes.
8	5	0.4940	0.4279	0.4996	4	11
9	10	0.5708	0.4944	0.4996	4 –3.9	11
10	15	0.5747	0.4978	0.4996	3.9–3.8	11 –10.9
11	20	0.5770	0.4997	0.4996	4 –3.6	11.1–11
12	25	0.5787	0.5012	0.4996	3.8–3.5	11.2–11
13	30	0.5789	0.5014	0.4996	3.6–3.7	11.2–10.8

For time curves see Fig. 1, above.

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From the above tables it is evident that (1) the maximum deposit has not been reached in ten minutes for 0.25 gram nor in fifteen minutes for 0.5 gram of material, but that fifteen and twenty-five minutes respectively are needed; (2) that the amount of lead calculated from the deposits is too large by 0.0005 gram in the former case and 0.0016-0.0018 gram in the latter.

In order to insure that these conclusions were correct and to ascertain in how far this method is accurate a series of experiments were made in which different weights of material were used. The amount of lead present was determined as sulphate as described above. The electrolyte and conditions for electrolysis were the same as for the experiments given in Tables I and II.

TABLE III.

No. expt.	Time, Min.	PbO_2 found.	Pb calc.	Pb present.	Error. Mg.	Error. Per cent.	Volts.	N. D_{100} amperes.
12	25	0.5787	0.5021	0.4996	+1.6	+0.32	3.8–3.5	11.2–11
13	30	0.5789	0.5014	0.4996	+1.8	+0.36	3.6–3.7	11.2–10.8
14	25	0.5781	0.5007	0.4992	+1.5	+0.30	4 –3.6	11.3–11.2
15	30	0.5780	0.5006	0.4992	+1 4	+0.28	3.6	11
5	15	0.2873	0.2488	0.2483	+0.5	+0.20	3.7–3.8	10.8–11
6	18	0.2873	0.2488	0.2483	+0.5	+0.20	3.9	11.2–11
7	15	0.2874	0.2489	0.2483	+0.6	+0.24	4	13
16	15	0.2885	0.2499	0.2496	+0.3	+0.12	3.8–3.7	11
17	20	0.2889	0.2502	0.2496	+0.6	+0.24	3.8	11
18[1]	180	0.2887	0.2501	0.2496	+0.5	+0.20	2.3–2.1	1.6– 1.5
19	15	0.1137	0.0985	0.0982	+0.3	+0.26	3.8–3.7	11 –11.2
20	16	0.1136	0.0984	0.0982	+0.2	+0.17	4 –3.7	11.4
21	17	0.0567	0.0491	0.0491	±0.0	±0.00	4 –3.7	11.5–11
22	16	0.0563	0.0488	0.0491	−0.3	−0.61	3 9–3.8	11.4–10.8
23	15	0.0569	0.0493	0.0491	+0.2	+0.41	3.9–3.6	11.2–11
24	15	0.0565	0.0489	0.0491	−0.2	−0.41	4 –3.6	11 –10.9
25	15	0.0567	0.0491	0.0491	±0.0	±0.00	3.8–3.6	11.2–11

By inspection it is evident that the results of determinations of different amounts of lead agree very well for each definite weight, but as shown by the error in milligrams, column 6, beginning with the smallest deposit of PbO_2 used, we get lead equivalents which are too high and the error gradually increases with the weight of the deposits until in the case of the deposits approximating 0.58

[1] 18 was made with a stationary cathode.

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gram PbO_2 the lead equivalent is on the average 1.5 mg. too high. This is exactly the opposite of what Hollard found, working with stationary electrodes and drying at 200° C. for fifteen minutes.

Determination No. 18 was made with a stationary cathode and it is in close agreement with the others of its class. It represents the manner in which Exner,[1] and subsequently Fisher and Boddaert[2] standardized their solutions, except that these chemists dried the deposit at 180° C. It is of interest to note the effect of increase of temperature upon this deposit.

TABLE IV.

Minutes heated.	Temperature.	Weight of deposit.
30	180°–190°	0.2895
30	180°–190°	0.2895
15	230°	0.2889
15	230°	0.2887
120	230°	0.2887

This led to a study of the weights of all the deposits at different temperatures, say at 180°-190°, as recommended by Classen, at 200° for fifteen minutes, as recommended by Hollard, and finally to constant weight at 230°, an idea taken from the work of Carnelley and Walker.

TABLE V.

No. of experiment.	Minutes heated.	Temperature.	Weight of deposit.	Pb present.	Pb/PbO_2 factor.
	30	180°–190°	0.5805		
	90	180°–190°	0.5805		
12	30	190°–210°	0.5799		
	120	190°–210°	0.5799		
	30	240°	0.5787		
	180	240°	0.5787	0.4996	0.8633
13	60	240°	0.5789		
	30	240°	0.5789	0.4996	0.8630
	30	200°	0.5788		
	30	200°	0.5788		
14	30	240°	0.5781		
	30	240°	0.5781	0.4992	0.8635
	30	200°	0.5788		
	30	200°	0.5790		
15	30	230°	0.5780		
	120	240°	0.5780	0.4992	0.8635
				Average,	0.8634

[1] J. Am. Chem. Soc., 26, 896.

[2] Z. Elektrochem., 10, 130.

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Further ignition for two hours at 270° C. did not alter the weights of these deposits. These results show that deposits approximating 0.578 gram PbO_2 are not really of constant weight until heated to 230° C.

In the same way deposits approximating 0.288 gram in weight were heated at different temperatures with the following results:

TABLE VI.

No. of experiment.	Minutes heated.	Temperature.	Weight of deposit.	Pb present.	Pb/PbO_2 factor.
5	15	230°	0.2878		
	60	230°	0.2873		
	60	230°	0.2873	0.2483	0.8641
6	30	230°	0.2873	0.2483	0.8641
7	60	200°–220°	0.2874		
	40	230°–250°	0.2873		
	140	240°	0.2874	0.2483	0.8640
16	30	200°	0.2885		
	30	200°	0.2885		
	30	230°	0.2885		
	30	230°	0.2885	0.2496	0.8651
17	30	200°	0.2889		
	30	200°	0.2889		
	30	230°	0.2889	0.2496	0.8640
18	See Table IV.		0.2887	0.2496	0.8646
				Average,	0.8643

These results show that deposits approximating 0.288 gram are constant at a lower temperature, namely, at 200° instead of 230°. They are not constant, however, when heated at this temperature for fifteen minutes, No. 5, but required thirty minutes, No. 16.

With the smaller deposits, 0.11-0.05 gram, the observed error was small and it was not considered necessary to introduce an analytical factor. For the same reason the minimum temperature for constant weight was not determined.

The following table shows the weights of these smaller deposits (1) after washing with absolute alcohol and absolute ether and (2) after drying at 230° to constant weight.

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TABLE VII.

No. of experiment.	(1)	(2)	Loss.
19	0.1147	0.1137	0.0010
20	0.1150	0.1136	0.0014
21	0.0570	0.0567	0.0003
22	0.0567	0.0563	0.0004
23	0.0569	.....	.....
24	0.0573	0.0565	0.0008
25	0.0569	0.0567	0.0002

These results show that there is little likelihood of the formation of a definite hydrated lead dioxide here and, moreover, it is impossible to use an analytical factor after drying just sufficiently to remove adhering water.

CONCLUSION.

From the above work it is evident that the electrolytic deposits of PbO_2 are too high unless heated at 200°-230° C., depending upon the weight of the deposits, and even then it is necessary to use an analytical factor, as was suggested by Hollard.

That this high weight is due to the formation and deposition of a higher oxide of lead than PbO_2 does not necessarily follow, unless proven by analysis, and accepting Schucht's analyses, this does not seem possible. It is more probable from Schucht's work that traces of water, adhering or included, are expelled with difficulty, at least the fact that the error increases with the density of the deposit might be advanced as an argument in favor of this view.

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DETERMINATION OF MERCURY FROM A SULPHIDE ELECTROLYTE USING A ROTATING ANODE.

In the usual course of analysis mercury is obtained in the form of sulphide. The determination of the metal in this form requires the use of a tared filter or crucible, and the operation requires care and considerable time.

It has already been demonstrated[1] that a solution of HgS in sodium sulphide will yield its mercury content readily to the electric current, the metal being deposited upon the cathode in a very satisfactory condition for washing, drying and weighing. The directions show that from such a solution, 0.1902 gram of metal can be deposited in five hours.

Now that it is possible to shorten the time necessary for the complete deposition of so many metals by using a rotating anode and a high current density it was thought that the application of these principles to the above electrolyte might afford interesting results.

Approximately 14 grams of mercuric chloride, purified by sublimation, were dissolved in water and, as is usually the case when this salt is purified this way, some mercurous chloride was present and did not dissolve. This was not filtered off, but an excess of ammonium sulphide was added to the solution which precipitated HgS from $HgCl_2$ and converted HgCl into HgS and Hg. The precipitate was allowed to settle and it was then washed by decantation with hot water until a portion of the liquid gave no test for chlorine with silver nitrate.

The precipitated HgS was then dissolved in 250 cc. sodium sulphide solution (sp. gr. 1.17), the free mercury from mercurous chloride filtered off, and the filtrate diluted to 1 liter.

Twenty-five cc. portions of this solution were used in the following experiments:

[1] Edgar F. Smith's "Electrochemical Analysis," 1902, p. 74.

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TABLE VIII.

No. of expt.	Time in minutes.	Hg found.	Na_2S(sp. gr. 1.17) in cc.	Volts.	N. D_{100} amperes.
1	10	0.1959	—	10.5–10	5 –6.3
2	10	0.2582	10	7 –6.8	6 –6.2
3	10	0.2576	10	10 –7.7	10.1–9.6
4	10	0.2554	20	5.3–5.7	6 –5.8
5	12	0.2596	10	7.5–7	6 –6.2
6	13	0.2601	10	6.7–6.6	6
7	15	0.2602	10	7 –6.6	6 –5.9
8	15	0.2571	10	9.3–7.1	6 –6.2
9	20	0.2604	10	7 –6.5	6
10	25	0.2605	10	6.9–6.4	6 –5.9
11	8	0.2538	10	6.8–6.7	6 –6.2
12	5	0.2198	10	7	6.1–6.2
13	2	0.1371	10	6 –6.6	6– 6.2

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In experiment No. 1, 25 cc. of the stock solution were pipetted into a platinum dish used as a cathode. The solution was then diluted to 115 cc. and heated to steaming. Upon heating, black HgS separated out upon the surface of the liquid and upon the sides of the dish. This solution was then electrolyzed, using a platinum spiral anode rotating about 500 times per minute. After stopping the experiment the HgS that had separated out at first had remained undissolved and this accounts for the low result.

To prevent this separation of HgS and still secure a hot electrolyte, boiling water was used to dilute the stock solution, but even then a slight separation of sulphide occurred. This was entirely prevented in No. 2 by adding 10 cc. sodium sulphide solution (sp. gr. 1.17) before diluting.

The dish was kept covered during the electrolysis with coverglasses, which were washed down every few minutes with water in order to wash back any of the electrolyte which may have splashed up and to keep the level of the solution above the deposit of metal, thus preventing any possible loss of the latter by evaporation.

In No. 3 the effect of a higher current density was tried without any apparent advantage. In No. 4 the use of a larger amount of sodium sulphide likewise gave no beneficial result.

The liquid siphoned off from Nos. 2, 3, 4, 5 and 8, when boiled with ammonium nitrate solution till all H_2S had been expelled,

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showed the presence of HgS, but with Nos. 6, 7, 9 and 10 no HgS could be detected.

No. 8 was made by diluting with cold water and it showed that it takes longer to get out the metal from a cold electrolyte.

Nos. 11, 12 and 13 were made to find out how much metal was deposited in two, five and eight minutes respectively in order to complete the data for the time-curve on page 9.

After each experiment the alkaline liquid was siphoned off without interrupting the current, fresh water being added as it was drawn off until the ammeter registered zero. The connection was then broken and the dish washed with absolute alcohol, absolute ether, warmed between the hands to remove last traces of ether, the outside of the dish wiped with a clean soft cloth and stood in a desiccator twenty minutes before weighing. After standing twenty minutes the deposit weighed the same as it did after standing twenty-four hours.

The mercury was dissolved off the dish with hot nitric acid (1 : 1) and after the metal had dissolved an insoluble film of platinum black remained upon the dish, showing that the mercury had penetrated the platinum, forming an amalgam with it. This dark film was removed after each experiment by polishing with rounded sea-sand and because of this the dish lost in weight on the average of 0.0025 gram for each experiment.

It is evident from the above results that this electrolyte affords an excellent medium for the rapid determination of this metal, which fact, once demonstrated, allows us to call attention to the work of Wallace,[1] who determined the mercury content of pure cinnabar by dissolving the mineral in sodium sulphide and electrolyzing the resulting solution. The results obtained in this way agreed excellently with those obtained by distillation with lime. The time required for complete deposition was three hours.

A specimen purchased from the Foote Mineral Co., Philadelphia, as California cinnabar, showed by distillation with lime the presence of 46.26 per cent. Hg.

Weighed samples of this pulverized ore were heated to boiling with 20 cc. sodium sulphide solution (sp. gr. 1.06) in a small beaker which was covered with a watch-glass.

[1] Edgar F. Smith's "Electrochemical Analysis," 1902, p. 74.

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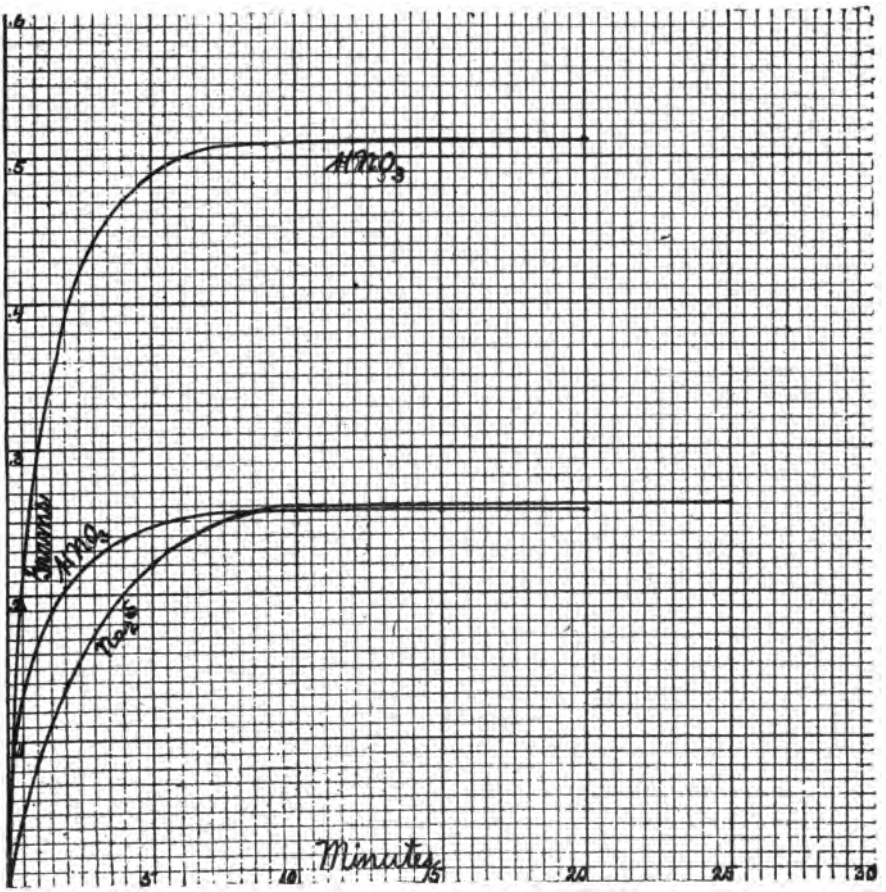

FIG. 2.—Rate of deposition of mercury.

The gangue was allowed to settle out and the supernatant liquid poured through a filter into a platinum dish. The gangue was treated with a second portion of 10 cc. sodium sulphide and allowed to settle, and the solution filtered as before. This operation was repeated a third time, using 40 cc. sodium sulphide altogether. In the cases where 0.5 gram of ore were used it was digested successively with 20 cc. portions, using 60 cc. in all. Finally, the gangue was washed twice by decantation with hot water and then thrown

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upon the filter, which was washed until the filtrate was neutral to litmus.

The solution obtained in this way was electrolyzed without heating and on this account it took longer than would be expected from the work on the rate of precipitation from this electrolyte (see No. 8, Table VIII), which is lower than the others of its class because the solution was electrolyzed cold.

TABLE IX.

No. of experiment.	Time in min.	Na_2S(sp.gr. 1.06). cc.	Ore.	Hg found.	Per cent.	Volts.	N. D_{100} amperes.
1	15	40	0.3007	0.1380	45.88	6.2–6.1	6 –6.2
2	20	40	0.3002	0.1393	46.40	6.3–5.7	6
3	25	40	0.3002	0.1395	46.46	6.9–5.7	6 –6.2
4	30	40	0.3004	0.1394	46.40	6.6–5.5	6.2–6.4
5	20	60	0.5003	0.2322	46.41	6 –5.1	6
6	25	60	0.5002	0.2321	46.40	5.6–4.9	6.2–6
7	30	60	0.5003	0.2325	46.46	5.8–5	6 –6.2

This shows precipitation is complete in twenty minutes, and no mercury could be detected in the liquid siphoned off by boiling with ammonium nitrate as above.

The gangue insoluble in sodium sulphide was dried, separated from the filter and ignited with lime to see if decomposition had been complete. No mercury could be detected on the sides of the glass tube in which the test was made.

The time necessary for the above analyses did not exceed one hour and thirty minutes from the time of weighing the ore until the weight of the deposit had been ascertained.

DETERMINATION OF MERCURY FROM A SOLUTION OF MERCUROUS NITRATE ACIDULATED WITH NITRIC ACID.

Mercury can be deposited readily from a solution of its nitrate or chloride acidulated with nitric acid. Classen and Ludwig[1] state that under ordinary temperatures this requires from twelve to sixteen hours. Later the time factor was cut down to four hours by heating the electrolyte to 70° C. and using higher current densities.

[1] Ber. chem. Ges., 19, 323.

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Exner,[1] using a rotating anode and high current density, was able to deposit 0.5 gram of metal in twelve minutes from a hot electrolyte. He says the platinum dish used as cathode lost 0.0006 gram in weight during three experiments. The electrolyte consisted of a solution of mercurous nitrate acidulated with 1 cc. of concentrated nitric acid.

Fischer and Boddaert,[2] following Exner's work, evidently used a solution of mercuric chloride acidulated with nitric acid, for they say that if the electrolyte is heated a loss of mercury, probably by volatilization of the chloride, takes place. They prevented this by starting with an electrolyte at ordinary temperature and by using a lower current density so that the temperature at the end of the electrolysis should not exceed 45° C. This took twenty minutes, or double the time that Exner found necessary.

The two following series of experiments were made to determine the rate of deposition of mercury from a solution of mercurous nitrate, using a rotating anode.

Electrolyte.—Twenty-five cc. mercurous nitrate solution; 1 cc. of concentrated nitric acid (sp. gr 1.17). Total dilution, 115 cc.

TABLE X.

No. of experiment.	Time in minutes.	Hg found.	Volts.	N. D_{100} amperes.
1	2	0.2040	6.5	7.4–7
2	4	0.2387	7.7–7.5	7.6–8
3	6	0.2477	7.9–8	7 –7.1
4	8	0.2559	7	7.2–6.9
5	10	0.2558	7 –7.4	7 –7.1
6	15	0.2561	7 –6.7	7.3–6.9
7	20	0.2558	7	7.4–7
8	20	0.2561	8.4–6.2	7.2

The liquid siphoned off from Nos. 4, 5, 6, 7 and 8 gave no test for mercury with ammonium sulphide. The electrolyte in No. 8 was not previously heated in order to see if there had been any loss of mercury in the other experiments. No difference was noted.

Electrolyte.—Fifty cc. mercurous nitrate solution; 1 cc. concentrated nitric acid (sp. gr. 1.17). Total dilution, 115 cc.

[1] J. Am. Chem. Soc., 25, 896.
[2] Z. Elektrochem., 10, 950.

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TABLE XI.

No. of experiment.	Time in minutes.	Hg found.	Volts.	N. D_{100} amperes.
9	2	0.3612	6 –7	7.1–7.2
10	4	0.4772	6.3–6.6	7.2
11	8	0.5077	6.7–6.6	7.3–7.1
12	10	0.5122	6.4–6.3	7.2–7.1
13	12	0.5121	7 –6.6	7.2–7
14	20	0.5119	6 –6.4	7.2–7

For time curves see Fig. 2 on page 17.

The liquid siphoned off from Nos. 12, 13 and 14 gave no test for mercury with ammonium sulphide.

The conditions of experiment were the same as recommended by Exner, and the results are a complete confirmation of his work except that a greater loss in weight by the platinum dish was noted. When the deposit was dissolved off the dish with hot nitric acid, the same dark film of platinum black was noticed as in the case of the deposits from the sulphide electrolyte. This was also removed by polishing with sand, but the loss in weight was not so great here, being on the average 0.0015 gram.

The cover-glasses were washed down every few minutes in order to replace any of the electrolyte that had splashed upon them and to keep the level of the electrolyte above the deposit of metal.

The time necessary for the deposition of 0.25 gram of mercury from this electrolyte is eight minutes and for 0.5 gram ten minutes.

The writer wishes to make this expression of appreciation to Dr. Edgar F. Smith for instruction in chemistry which made this investigation possible, and for suggestions and advice in carrying it out.

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